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**Temporal Variations of O<sub>3</sub> and NO<sub>x</sub> in the Urban  
Background Atmosphere of the Coastal City Jeddah,  
Saudi Arabia**

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36

37 **ABSTRACT**

38 Ozone is a pollutant of major concern because of its well recognised effects upon human health and  
39 crop yields. This study analyses in depth a new dataset for ozone from Jeddah, a coastal city in  
40 Saudi Arabia within the Middle Eastern region, for which very few ozone data are currently  
41 available, collected between March 2012 and February 2013. The measurements presented include  
42 NO, NO<sub>2</sub> and ozone as well as relevant meteorological variables. The data show a marked seasonal  
43 variation in ozone with highest concentrations in the summer months and lowest average  
44 concentrations in the winter. Concentrations also show a substantial difference between weekdays  
45 and weekends, with higher NO and NO<sub>2</sub> on weekdays, but lower concentrations of ozone. Plots of  
46 total oxidant versus NO<sub>x</sub> concentration indicate background concentrations of ozone (at zero NO<sub>x</sub>)  
47 ranging from 38.2 ppb in January to 59 ppb in May consistent with the northern hemisphere spring  
48 maximum in ozone concentrations. The slope of total oxidant/NO<sub>x</sub> varies from 0.13 in March to  
49 0.68 in August. The two summer months of July and August are anomalous with slopes of around  
50 double that of other months, suggesting a higher efficiency of ozone production at lower primary  
51 pollutant concentrations arising from much reduced daytime traffic. A substantial  
52 weekend/weekday difference in ozone which is higher at weekends appears to be attributable to  
53 lower daytime traffic activity and hence reduced emissions of NO<sub>x</sub> to a “NO<sub>x</sub>-saturated”  
54 atmosphere.

55

56 **Keywords:** Ozone; oxides of nitrogen; Saudi Arabia; total oxidant; weekend effect;  
57 meteorological parameters

58

59

## 1. INTRODUCTION

Tropospheric photochemical reactions transform primary air pollutants into secondary pollutants. Photochemical oxidants are amongst the most important products formed during these reactions. Among these, ozone ( $O_3$ ) is particularly important because it is a major constituent of photochemical smog and has deleterious effects on public health, various natural materials, manufactured goods, vegetation and forests.  $O_3$  is one of the important greenhouse gases and contributes to global warming and climate change (IPCC, 2007). Moreover, it plays a critical role in tropospheric chemistry and is considered one of the key species affecting the chemical properties of the atmosphere since it is a key precursor of hydroxyl radical (OH) which controls the oxidizing power of the lower atmosphere (Thompson, 1992).

Ground level  $O_3$  may arise from troposphere/stratosphere exchange, as well as from photochemical reactions taking place within the troposphere (Monks, 2000). It is formed in the troposphere through a series of complex photochemical reactions among its anthropogenic precursors, which include industrial and vehicular emissions of nitrogen oxides ( $NO_x = NO + NO_2$ ) and volatile organic compounds (VOCs) in the presence of sunlight. In urban areas, the relation between photochemical  $O_3$  production and the concentration of its precursors is not linear; it depends upon the concentrations of  $NO_x$  and VOCs, the ratio of  $NO_x$  to VOCs, and the intensity of solar radiation (Kleinman et al., 2001; Zhang et al., 2004; Tie et al., 2006). In some cases,  $O_3$  formation is controlled almost entirely by  $NO_x$  and is largely independent of the amount of VOC ( $NO_x$ -sensitive), while in other cases, it increases with increasing VOC (VOC-sensitive) (Sillman, 1999). Increasing the concentration of VOCs always increases  $O_3$  formation, whereas increasing  $NO_x$  leads to more or less  $O_3$ , depending on the prevailing ratio between [VOCs] and [ $NO_x$ ] (Guicherit and Roemer, 2000; Sadanaga et al., 2003).  $NO_x$  emissions are mainly responsible for  $O_3$  formation in rural areas, whereas VOCs are primarily responsible for  $O_3$  formation in urban areas (EEA, 1998).

Nitrogen monoxide (NO) is emitted from combustion processes and is short lived because it is oxidized to produce  $NO_2$  which plays a major role in  $O_3$  production. In the presence of sunlight,  $O_3$  is produced by the reaction of an oxygen molecule ( $O_2$ ) with a ground state oxygen atom (O), which originates from the photolysis of nitrogen dioxide ( $NO_2$ ) by solar radiation. Once formed,  $O_3$  quickly reacts with NO regenerating  $NO_2$  in the absence of VOCs. This, so-called 'null cycle', does not lead to a net production or destruction of  $O_3$ . The presence of VOCs in the atmosphere interacts with this mechanism through reactions driven by the hydroxyl radical (OH), leading to oxidation of NO and therefore, to accumulation of  $O_3$  (Seinfeld and Pandis, 1998). VOC oxidation reactions are

mainly induced by OH radicals leading to the production of hydroperoxy ( $\text{HO}_2$ ) and organic peroxy ( $\text{RO}_2$ ) radicals. These radicals oxidize NO to  $\text{NO}_2$  without consumption of  $\text{O}_3$  and the photolysis of the resulting  $\text{NO}_2$  by sunlight leads to an increase the accumulation of  $\text{O}_3$  (Seinfeld and Pandis, 1998).

Variations in  $\text{O}_3$  concentration are controlled by a number of processes including photochemistry, physical/chemical removal, and transport. Precursor emissions ( $\text{NO}_x$  and VOCs) can lead to elevated levels of surface  $\text{O}_3$  locally and downwind and cause large diurnal, day-to-day, seasonal and year-to-year variations in  $\text{O}_3$  levels as a result of complex meteorological influences and photochemical mechanisms (Solomon et al., 2000). Meteorological conditions have been shown to play an important role in  $\text{O}_3$  formation and transport (Laurila, 1999; Thompson et al., 2001). High levels of  $\text{O}_3$  might be registered within a city or at a distance downwind due to the high emissions of  $\text{O}_3$  precursors in urban areas (Garcia et al., 2005).  $\text{O}_3$  concentrations increase also with solar radiation and temperature elevation (Tecer et al., 2003).

The  $\text{O}_3$  “weekend effect” is a common phenomenon of  $\text{O}_3$  behaviour in the urban atmosphere: higher  $\text{O}_3$  concentrations may occur on weekends compared to weekdays despite lower concentrations of  $\text{O}_3$  precursors at weekends. This phenomenon has been recognised in several countries (Marr and Harley, 2002b; Qin et al., 2004; Paschalidou and Kassomenos, 2004; Jimenez et al., 2005; Gao et al., 2005; Riga-Karandinos and Saitanis, 2005; Sakamoto et al. 2005; Pudasainee et al. 2006; Sadanaga et al., 2008; Khoder, 2009). The mechanisms for the weekend effects on  $\text{O}_3$  formation are still not well understood. However, several photochemical modeling studies and a wide range of environmental analyses (Marr and Harley, 2002a; Yarwood et al., 2003; Blanchard and Tanenbaum, 2003; Heuss et al., 2003; Lawson, 2003) have suggested that the primary cause of higher  $\text{O}_3$  on weekends is the reduction in  $\text{NO}_x$  emissions in a VOC-limited chemical regime. Marr and Harley (2002a, b) proposed that less absorption of sunlight due to lower fine-particle concentrations at weekends, resulting in enhanced  $\text{O}_3$  formation might be a cause for the weekend  $\text{O}_3$  effect. Qin et al. (2004) suggested that VOC sensitivity combined with a decrease of  $\text{NO}_x$  emissions at weekends was the cause.

The recent rapid increase in urbanization, industrialization and human activities has important impacts on air quality in Jeddah city. As a result, the emissions of  $\text{O}_3$  precursors ( $\text{NO}_x$  and VOCs) have significantly increased. Therefore, the problem of pollution has been shifted towards the so-called photochemical pollutants. The formation of these pollutants in the Jeddah atmosphere is

128 facilitated by the local climatic conditions (high temperature, intense solar radiation, clear sky),  
129 especially in the summer season. Therefore, it is very important to evaluate the diurnal and seasonal  
130 variations of ground level O<sub>3</sub> concentrations and their association with NO<sub>x</sub> and meteorological  
131 parameters. Moreover, the difference in O<sub>3</sub> concentrations between weekdays and weekends is also  
132 considered. This will help in understanding the atmospheric chemistry over the semitropical region  
133 within which very few studies have been conducted, and in informing a strategy to control ground  
134 level O<sub>3</sub> and other photochemical oxidants and their build-up in smog episodes in the future. A  
135 recent complementary study has examined spatial patterns of NO<sub>x</sub> and O<sub>3</sub> (Hassan et al., 2013).

136

## 137 **2. MATERIALS AND METHODS**

### 138 **2.1 Study Area**

139 Jeddah is the most significant commercial centre and the second largest city in the Kingdom of  
140 Saudi Arabia. It houses more than 3.4 million inhabitants. The city is surrounded by mountains in  
141 the north-east, east and south-east. The growth of the city over the last thirty years has been rapid  
142 and diverse, and continues to date (Saudi Network, 2008). Unfortunately, due to lack of awareness  
143 and proper regulations, these development activities have been accompanied by environmental  
144 degradation, and over the years the air quality has progressively deteriorated. Like almost  
145 everywhere else in the world, the Jeddah environment and its citizens' health are affected by both  
146 mobile and stationary sources. More than 1.4 million vehicles are running in the streets of Jeddah  
147 city (Khodeir et al., 2012). Vehicle fuels used in Jeddah are mainly unleaded gasoline and diesel.  
148 The stationary sources in this city include an oil refinery, a desalinization plant, a power generation  
149 plant and several manufacturing industries.

150

### 151 **2.2 Sampling Sites and Periods**

152 The sampling site for monitoring of NO, NO<sub>2</sub>, NO<sub>x</sub>, O<sub>3</sub> and meteorological parameters was chosen  
153 in an urban background area of Jeddah city (Jamea district), located in the southeast of the city  
154 (Figure 1). The geographic co-ordinates of this site are 21.4869°N; 39.2517°E and the altitude is  
155 38.7 m asl. Most of the air pollutant emissions arise from the surrounding traffic activities. The site  
156 is 105 metres from the nearest road, and 1700 metres from the closest major highway.

157

158 Sampling took place from March 2012 to February 2013. All times cited are local time (UTC+3).

159

160

## 161    **2.3        Measurements and Instrumentation**

162    Sampling was carried out at a height of 3.5 m for gaseous air pollutants and 6.7 m for  
163    meteorological parameters above the ground level. NO, NO<sub>2</sub>, NO<sub>x</sub>, O<sub>3</sub> and meteorological  
164    parameter data were monitored continuously from March 2012 to February 2013. A UV Absorption  
165    Ozone Analyzer (Model 400E, Teledyne Technologies Company, San Diego) was used to monitor  
166    ozone concentration. It is a microprocessor-controlled analyzer that uses a system based on the  
167    Beer-Lambert law for measuring low ranges of ozone in ambient air. Accurate measurements are  
168    obtained in the ranges of 0-100 ppb to 0-10 ppm, with a lower detection limit of < 0.6 ppb. A  
169    chemiluminescence NO/NO<sub>2</sub>/NO<sub>x</sub> analyzer (Model 200E, Teledyne Technologies Company, San  
170    Diego) was used to monitor NO, NO<sub>2</sub> and NO<sub>x</sub> concentrations. It uses the proven  
171    chemiluminescence detection principle, coupled with state-of-the-art microprocessor technology to  
172    provide measurements of NO/NO<sub>2</sub>/NO<sub>x</sub> in the ranges of 0-50 ppb to 0-20,000 ppb full scale, with a  
173    lower detection limit of < 0.4 ppb. Ozone calibration was checked with an ozone generator with  
174    that of NO/NO<sub>2</sub>/NO<sub>x</sub> by seven point dilution of a standard gas mixture using mass flow controllers.  
175    Quality control checks were performed every three days including inspection of the shelter and  
176    instruments as well as zero concentration check, precision and span checks. The filter was replaced  
177    once every two weeks and calibration was conducted every month. The O<sub>3</sub>, NO and NO<sub>2</sub>  
178    concentrations were recorded every one minute.

179

180    Air temperature, relative humidity, windspeed and direction were measured continuously using  
181    Lufft WS600-UMB Compact Weather Station, simultaneously with measurements of atmospheric  
182    pollutant concentrations. Solar radiation was measured continuously using a solar radiation sensor  
183    (Vantage Pro2<sup>TM</sup> Accessories, Davis Instruments, USA).

184

185    Daylight hours are 6am to 7pm in spring and summer, 6am to 6pm in autumn and 7am to 6pm in  
186    winter. Traffic levels remain high throughout the day, and extend into late evening as many  
187    facilities remain open.

188

## 189    **3.        RESULTS AND DISCUSSION**

### 190    **3.1        Influence of Meteorological Parameters on O<sub>3</sub> Concentration**

191    Data are disaggregated by season, i.e. winter (DJF), spring (MAM), summer (JJA) and autumn  
192    (SON). Surface hourly air temperature is highest during summer and varied from 27 °C to 43 °C.  
193    In the winter season, the temperature profile is at a minimum and varies from 18 °C to 37 °C.

194 Figure 2 shows the monthly variation of average temperature (Figure 2a), relative humidity (Figure  
195 2b) and wind speed (Figure 2c) during the study period. Monthly average ozone concentrations  
196 both for all hours and for daytime hours appear in Figure 3.

197

198 O<sub>3</sub> followed a close relationship with solar radiation; and hence surface temperature. The highest  
199 daytime average O<sub>3</sub> concentration (44.1 ppb) was observed in August with the highest average air  
200 temperature (35 °C) and a minimum of 23.5 ppb in December (26°C). Hourly O<sub>3</sub> concentration was  
201 weakly but significantly correlated with temperature for hourly data ( $r = 0.33$ ,  $p < 0.001$ ) in the  
202 present study. The favourable meteorological conditions (clear sky, high temperature and light  
203 winds) have a great influence on O<sub>3</sub> levels (Vecchi and Valli, 1999). The separate influences of  
204 temperature and solar radiation are too closely linked to allow disaggregation; neither shows a strong  
205 seasonal cycle (see Figures 2(a) and (d)).

206

207 Average relative humidity was observed to be maximum in autumn and winter seasons while  
208 minimum in summer. It varied from around 52% in winter to about 40% in summer (Figure 2b) and  
209 thus exhibits a significant negative correlation for hourly data ( $r = -0.27$ ,  $p < 0.001$ ) with O<sub>3</sub>  
210 concentration. Therefore, the negative relationship arises simply from the fact that relative humidity  
211 is low in summer, when ozone production is most efficient.

212

213 Positive correlation ( $r = 0.78$ ,  $p < 0.001$ ) was found between hourly O<sub>3</sub> and wind speed. This is  
214 quite a strong relationship which seems unlikely to be related to the seasonal pattern in wind speed  
215 (Figure 2(c)), and is probably explained by low NO<sub>x</sub> concentrations due to enhanced dilution at high  
216 wind speed, borne out by a strong reduction in both NO and NO<sub>2</sub> concentrations with increasing  
217 wind speed (Figure S1). Pollution roses also show an increasing gradient of NO<sub>x</sub> gases with winds  
218 when moving from NW to SE, and inverse behaviour for ozone. This probably reflects stronger  
219 average winds from the NW sector diluting NO<sub>x</sub> emissions, rather than proximity of local sources.

220

### 221 **3.2 Monthly Variations of O<sub>3</sub> and NO<sub>x</sub> Concentrations**

222 The highest monthly daytime (8 h from 09:00 to 17:00) and daily average O<sub>3</sub> concentrations were  
223 observed in the summer, especially August, with values around 45 ppb and 30 ppb, respectively  
224 (Figure 3). The daily concentration had another maximum in March with a value around 26 ppb.  
225 The lowest concentrations were observed in the cooler months of October – February with values as  
226 low as 18 ppb and 24 ppb for the daily and daytime concentrations, respectively. Figure S2 shows



seasonally averaged data. In the present study, the average daytime O<sub>3</sub> concentrations (8 h) during the four seasons fell below the European Union air quality standard (60 ppb, 8 h average). These are also below the National Ambient Air Quality Standards (NAAQS; 75 ppb, 8 h average) set by the US Environmental Protection Agency. However, 20.6% of daytime 8-hourly ozone concentrations exceeded 50 ppb, and 3.4% exceeded the EU standard of 60 ppb. In the case of hourly concentrations, 7.3% of daily maximum hourly concentrations exceeded 60 ppb and 0.2% exceeded 75 ppb.

234

The monthly variation of mean daytime, nighttime and daily NO and NO<sub>2</sub> concentrations during the period of study are graphically presented in Figure 4. The highest daytime average NO and NO<sub>2</sub> concentrations were observed in May, whereas the lowest concentrations were observed in July and August. The mean daytime, nighttime and daily concentrations of NO and NO<sub>2</sub> during the four seasons are graphically presented in Figure S3. The average concentrations of NO<sub>2</sub> in daytime and nighttime were similar, except in summer where the nighttime average concentration was higher than the daytime. On the other hand, the daytime concentration of NO was higher than the nighttime, except in summer where the nighttime average concentration was higher than the daytime. Data appear in Table S2. Because of high temperatures in daytime during the summer season in Jeddah city and the official days-off of government institutions, schools and colleges, most of the people stay home, and consequently the density of traffic during daytime is decreased. Therefore, low concentrations of NO<sub>2</sub> and NO are observed in daytime. On the other hand, after sunset the weather becomes more suitable for going out for shopping and travelling, and the traffic continues to flow until about midnight on weekdays. The traffic continues after midnight on Fridays and even longer until morning during Ramadan (20th July to 18th August). This led to greater emissions of NO<sub>x</sub> at nighttime than daytime, and consequently the levels of these pollutants were higher at nighttime compared to daytime. Ratios of NO<sub>2</sub>/NO<sub>x</sub> are higher in the summer months (Figure 5) favouring higher ozone concentrations.

253

VOC are an important ozone precursor, but were not measured comprehensively in this study. However BTEX compounds, which contribute substantially to ozone formation were measured, and are being reported elsewhere (Alghamdi et al., 2014). Concentrations were broadly comparable with those of other cities and were highest overall in spring and summer. Although their potential for ozone formation is greatest in these seasons, it appears probable that NO<sub>x</sub> concentrations are a greater determinant of ozone through the reaction of ozone with NO.

260

### 261 3.3 Diurnal Variation of O<sub>3</sub> and NO<sub>x</sub> Concentrations

262 The study of diurnal variations of air pollutants can provide valuable information about the sources,  
263 transport and chemical formation/destruction effects of such pollutants. In addition, the diurnal  
264 variations have a major influence on exposure levels at sites nominally exposed to the same  
265 regional ozone distribution. The physical and chemical mechanisms which give rise to diurnal  
266 variations are detailed so that sites can be screened for different diurnal behavior characteristics  
267 (Derwent and Kay, 1988). The shapes of O<sub>3</sub> cycles are strongly affected by the levels of its  
268 precursors (NO<sub>x</sub> and VOCs) as well as the meteorological conditions (temperature and solar  
269 radiation (Alvim-Ferraz et al., 2006; Pudasainee et al., 2006; Khoder, 2009). The diurnal variations  
270 in O<sub>3</sub> concentrations during the period of study are graphically presented in Figure 6. From this  
271 figure, it can be seen that the O<sub>3</sub> diurnal variation of each season showed a similar pattern, but the  
272 magnitudes of variations were different. O<sub>3</sub> concentrations reached a maximum during daytime and  
273 a minimum in the nighttime during all four seasons. The diurnal pattern of O<sub>3</sub> for each season is  
274 characterised by a maximum concentration in the afternoon. Its variation in different seasons  
275 generally coincides with the amount of solar radiation where O<sub>3</sub> reaches a peak value in the  
276 afternoon hours, and then continuously decreases until midnight. Rates of rise and fall are  
277 described in Table S1. A uni-modal O<sub>3</sub> peak is seen for all seasons, with highest O<sub>3</sub> levels in  
278 summer followed by spring, then autumn and lowest levels in the winter season. The broad peak  
279 with higher amplitude of O<sub>3</sub> during daytime in the summer season is attributed to higher  
280 temperature, higher solar radiation intensity as well as the longer sunlight hours, which are the  
281 favourable conditions to power the photochemical reactions, and higher NO<sub>2</sub>/NO<sub>x</sub> ratios resulting in  
282 high levels of O<sub>3</sub>. Minimum values of O<sub>3</sub> concentrations appear in the nighttime and early morning  
283 hours (near sunrise). The time of sunrise is a turning point of diurnal O<sub>3</sub>. The O<sub>3</sub> concentration rises  
284 gradually just after the sun rises and reaches maximum levels at 1400- 1600 hours in winter and  
285 1300-1400 hours in spring, summer and autumn seasons (Figure 6). After that time, O<sub>3</sub>  
286 concentrations decrease progressively until evening, and then keep decreasing more gradually,  
287 maintaining low values over night hours due to lack of solar radiation. O<sub>3</sub> production rate increases  
288 at low NO<sub>x</sub> until a maximum is reached and then decreases at high NO<sub>x</sub> (Sillman et al., 1990). This  
289 pattern occurs because high NO<sub>x</sub> promotes removal of OH radicals by the reaction of OH with NO<sub>2</sub>  
290 (Zhang et al., 2004). On the other hand, as the sun goes down in the evening and nighttime, the  
291 photochemical processing of O<sub>3</sub> is halted due to the absence of the photochemical reactions, and the  
292 O<sub>3</sub> that remains in the atmosphere is then consumed by deposition (Colbeck and Harrison, 1985)  
293 and/or reaction with NO which acts as a sink for O<sub>3</sub> (Dueñas et al., 2002). The decrease in O<sub>3</sub>  
294 during the early morning hours of the day at 0700–0800 h local time in winter, spring and autumn  
295 and at 0200 h local time in summer (Figure 6) is mainly due to the increase in traffic flow (rush

hours) and fresh NO emissions in all seasons. Measurements of traffic flow on a major North-South highway in Jeddah (Melibari, 2011) show a minimum at around 4 am followed by a rush-hour peak at 7 am, slightly reduced levels of traffic from 8 am to 4 pm, followed by an evening peak around 6 pm and high traffic levels until midnight, declining rapidly thereafter. Such a pattern, modified by better atmospheric mixing during daytime is seen in NO<sub>x</sub> concentrations in Spring, Autumn and Winter (Figure 9).

302

Diurnal variations in NO and NO<sub>2</sub> concentrations during the period of study are graphically presented in Figure 6. From this figure, it can be seen that the hourly concentrations of NO increased from 0600 to 0800 hours in spring, autumn and winter and from 0000 to 0200 and 0500 to 0600 hours in summer (Figure 6a), then decreased in mid-day time. The apparently anomalous behaviour in summer results from human activity occurring mainly during nighttime hours when air temperatures are lower. After that time, the concentration increases again in the evening. Data appear in Table S3. The diurnal behavior of NO<sub>2</sub> was similar to that of NO, with a slightly different pattern (Figure 6). The diurnal cycles of these pollutants are related to the transportation/work cycle. During the morning time, the increase in the emission rate from traffic, accompanied by poorer dispersive conditions due to the shallower boundary layer, lead to an increase in the concentrations of NO<sub>x</sub>. On the other hand, the lower concentrations of NO and NO<sub>2</sub> during mid-day time may be due to the better dispersion caused by increased convective activity. Moreover, the higher temperature and solar radiation intensity during midday leads to increases in the photochemical reactions and consequently increases in the chemical loss of these pollutants. The high levels of NO during the morning hours in winter result in low concentrations of O<sub>3</sub> due to the rapid reaction between O<sub>3</sub> and NO. Apart from this, it is difficult to disentangle the effects of the various influencing factors.

320

Many facets of the data are comparable with those reported by Mavroidis and Ilia (2012) for urban background and suburban background sampling stations in Athens. Ozone in Jeddah shows a minimum during the morning rush hour, and an afternoon maximum (Figure 6), in reverse cycle to that of NO<sub>x</sub>, as in Athens. Daytime ozone concentrations (Figure S1) show a similar seasonal cycle in both cities.

326

### 3.4 Concentrations of Total Oxidant (O<sub>x</sub>)

Valuable insights into processes affecting ozone can be gained from application of the approach pioneered by Clapp and Jenkin (2001). This involves plotting the sum of ozone and nitrogen

330 dioxide (referred to as  $O_x$ ) against the concentration of  $NO_x$  (Figure 7). The concentration of  $O_x$  at  
331 zero  $NO_x$  is the regional tropospheric ozone background and appears as the intercept in the plot.  
332 The gradient of  $[O_x]/[NO_x]$  reflects sources of oxidant that increase with  $NO_x$ , which might include  
333 primary emissions of  $NO_2$ , or photochemical formation of ozone. Plots were conducted for each  
334 month of daytime data.

335

336 The oxidant intercept, or background ozone (Figure 7) ranged from 38.2 ppb in January to 59.0 ppb  
337 in May. This variation appears to be consistent with the spring maximum normally observed in  
338 northern hemisphere surface ozone measurements (e.g. Monks, 2000) and reported by Clapp and  
339 Jenkin (2001) in their UK dataset. These concentrations are higher than most concentrations  
340 measured in Jeddah, due to NO-related suppression of ozone in the city. The slope also shows  
341 substantial variation, from 0.13 in March to 0.68 in August. The two summer months of July and  
342 August are notably different from the other months, with slopes of around double the magnitude.  
343 This is consistent with the high average summer ozone concentrations seen in Figure S2. As the  
344 seasonal variation in solar radiation (Figure 2) is not great, it seems likely that this increase in  
345 daytime ozone may result predominantly from increased efficiency of ozone production at the lower  
346  $NO_x$  concentrations seen in Figure S3. The alternative explanation of an increased  $NO_2/NO_x$  ratio  
347 in residual traffic emissions in summer seems unlikely.

348

### 349 **3.5 Weekend/Weekday Variations in $NO$ , $NO_2$ , $NO_x$ and $O_3$ Concentrations**

350 The formation and destruction mechanisms of  $O_3$  determine the ground level  $O_3$  concentration. The  
351 differences in  $NO_x$  and  $O_3$  concentrations during the days of the week are observed mainly within  
352 areas with an influence from urban emissions, with lower  $NO_x$  levels and higher  $O_3$  values at  
353 weekends than on weekdays. This is caused by weekly changes in emissions from human activities.  
354 This emission-concentration relationship at urban, suburban and rural sites is open to different  
355 interpretation (Jenkin et al., 2002; Fujita et al., 2003; Stephens et al., 2008). In regions where  
356 weekday and weekend  $O_3$  values are approximately the same, the processes of background or long-  
357 range transport dominate, while sites dominated by regional or local anthropogenic  $O_3$  production  
358 present weekday-weekend differences (Heuss et al., 2003). So, a study of weekday and weekend  
359 differences in  $O_3$ - $NO_x$  levels is a valuable indicator of whether  $O_3$  has its origin in local  
360 photochemical production or in transport processes. In Jeddah, weekdays are taken from Saturday  
361 to Thursday while weekend is Friday (an Islamic custom). In order to study the weekend effect in  
362 the study area,  $O_3$  and  $NO_x$  daily evolution was examined on weekdays and at weekends in all four

363 seasons, as well as the daily average difference between weekend and weekdays (weekend minus  
364 weekdays).

365

366 The diurnal variations in NO and NO<sub>2</sub> concentrations on the weekdays and weekends (Fridays) and  
367 the weekday/weekend concentration ratios during the four seasons are graphically presented in  
368 Figure 8. The patterns of hourly variations in NO concentrations, i.e. the trend for increases or  
369 decreases, were similar during the weekdays and Fridays (except in Spring), with highest levels on  
370 the weekdays. NO<sub>2</sub> in ambient air originates mainly from the atmospheric oxidation of primary NO.  
371 The trend of the hourly concentration of NO<sub>2</sub> for increases or decreases during the weekdays and  
372 Fridays was also similar, with highest levels on the weekdays. The lower levels of NO and NO<sub>2</sub> at  
373 weekends (Fridays) are attributed to the reduction in the emission of these pollutants due to lower  
374 traffic density.

375

376 The reduction in traffic density and consequently vehicle emissions on weekends compared with  
377 weekdays is used to examine the linkages between emitted O<sub>3</sub> precursors and ground-level O<sub>3</sub>  
378 production. The phenomenon of a weekend effect on O<sub>3</sub> occurs when O<sub>3</sub> concentrations tend to be  
379 higher during weekends compared to weekdays in some areas, despite the fact of lower emissions of  
380 O<sub>3</sub> precursors (NO<sub>x</sub> and VOCs) during weekends. The ground-level O<sub>3</sub> concentration over the urban  
381 areas of Jeddah city depends on photochemical production of O<sub>3</sub> related to NO<sub>x</sub> concentration.  
382 Vehicle traffic is the major source of NO<sub>x</sub> emission at the studied urban site, where it is assumed  
383 that the weekend traffic density is lower than on weekdays due to the official days-off of  
384 government institutions, schools and colleges. However, in spite of low weekend NO<sub>x</sub> emissions, an  
385 elevated O<sub>3</sub> concentration was observed at the study site. Figure 9 shows the diurnal variations in  
386 NO<sub>x</sub> and O<sub>3</sub> concentrations at the weekdays and weekends (Fridays) and the difference between  
387 weekends and weekdays (weekends minus weekdays) during the period of study. The O<sub>3</sub>  
388 concentration on weekends was greater than weekdays during all four seasons.

389

390 The occurrence of a weekend O<sub>3</sub> effect was determined by the differences in O<sub>3</sub> concentration  
391 between weekend and weekdays. Blanchard and Fairley (2001) and Fujita et al. (2003) classified  
392 the criteria used to identify the status of the weekend effect into three categories: a) intense  
393 weekend effect if O<sub>3</sub> difference is > 15 ppb; b) moderate weekend effect if O<sub>3</sub> difference is 5-15  
394 ppb; and c) no weekend effect if O<sub>3</sub> difference is < 5 ppb. Using the above criteria, it can be seen  
395 that a moderate weekend effect was observed in all seasons. The mean hourly daytime difference  
396 between weekends and weekdays (weekends minus weekdays) ranged from 8.2 ppb to 16.2 ppb in

397 spring, 5.1 ppb to 8.8 ppb in summer, 4.2 ppb to 8.5 ppb in autumn, and 4.6 ppb to 13.4 ppb in  
398 winter (Figure 9 and Table S4). The weekend O<sub>3</sub> effect is significant in spring and winter.  
399 Meteorological conditions are also responsible to some extent for an intense weekend O<sub>3</sub> effect on a  
400 seasonal basis; however, it appears that differences in concentrations of O<sub>3</sub> precursors (NO<sub>x</sub> and  
401 VOC) are a major cause for the weekend O<sub>3</sub> effect in the study area. At traffic influenced sites,  
402 increased vehicular traffic density from Saturday to Thursday leads to increased NO emission  
403 which is responsible for decreased O<sub>3</sub> concentrations on weekdays compared to weekends due to  
404 the rapid reaction of NO with O<sub>3</sub>. Hence the weekend effect on O<sub>3</sub> is attributable to the decreased  
405 local emission of NO on weekend mornings which consumes less O<sub>3</sub>, and the latter cannot be  
406 further depleted during the daytime (Atkinson-Palombo et al., 2006). In consequence, the  
407 accumulation of O<sub>3</sub> is increased during the weekend daytime. The different reduction rates for the  
408 emissions of NO and VOCs during weekends (Altshuler et al., 1995) and consequently the  
409 prevailing ratio between [VOCs] and [NO<sub>x</sub>] may lead to increased O<sub>3</sub> at the weekend. The weekend  
410 O<sub>3</sub> phenomenon depends largely on differences in NO<sub>x</sub> concentration between weekday and  
411 weekend; lower NO levels and VOC emissions on weekend mornings consume less O<sub>3</sub> which  
412 accumulates later by photochemical reactions (Pudasainee et al., 2006) which may be more efficient  
413 in a lower NO<sub>x</sub> environment. Khoder (2009) also found many sites in Cairo with elevated O<sub>3</sub> on  
414 weekends when traffic and O<sub>3</sub> precursor levels were substantially reduced. Moreover, the relative  
415 increase in solar radiation intensity which results from the lower concentrations of fine particles at  
416 weekends due to the lower traffic density can lead to an increase in the photochemical formation of  
417 O<sub>3</sub> at weekends (Marr and Harley, 2002a, b). O<sub>3</sub> levels in the ambient air increased when emissions  
418 of NO<sub>x</sub> decreased (Heuss et al., 2003; Bernstein et al., 2004; Sadanaga et al., 2008; Roberts-Semple  
419 et al., 2012). Similar observations were made in a potential non-attainment area of Cincinnati, Ohio  
420 where a reduction in NO emissions contributed to an increase in local O<sub>3</sub> (Torres-Jardon and  
421 Keener, 2006).

422

423 It is clear from the data that concentrations of NO<sub>x</sub>, and especially NO are substantially lower at the  
424 weekend than on weekdays. This is also the case during daytime in the summer season. It is unclear  
425 to what extent VOC concentrations decrease as there are no data, or what compositional changes  
426 may occur between weekdays and the weekend. Qin et al. (2004), working in southern California  
427 also reported a reduction in NO<sub>x</sub> at weekends, accompanied by an increase in ozone at most sites.  
428 VOC concentrations were reduced, but the mixture composition remained unchanged. It seems  
429 probable that motor vehicles are the main local source of VOC in Jeddah and that a similar situation  
430 prevails. If so, the main driver of the weekday-weekend effect and summer increase in ozone seems

likely to be the reduction in NO emissions and its effect upon the photostationary state through an increase in NO<sub>2</sub>/NO<sub>x</sub> ratio accompanying a reduced titration of ozone by NO. This reflects an atmosphere which is effectively “NO<sub>x</sub>-saturated” with respect to ozone formation. It also seems likely that ozone production efficiency is enhanced by the reduction in NO<sub>2</sub> and VOC levels, as these are major sinks for the key free radical species involved in conversion of NO to NO<sub>2</sub> without consumption of ozone.

437

#### 4. CONCLUSIONS

This is to our knowledge the most comprehensive analysis of an ozone dataset from a country of the Middle Eastern region. The concentrations of ozone are overall unexceptional for a polluted atmosphere, and some facets of the data are very similar to those in other parts of the world, whilst some are less so. An analysis of the total oxidant data following the method of Clapp and Jenkin (2001) reveals a typical northern hemisphere spring maximum in ozone although the background levels are exceptionally high for a low altitude site at over 50 ppb (Parrish et al., 2012). This may represent enhanced formation of ozone in background air due to the high photochemical reactivity of the region or enhanced vertical transport of stratospheric ozone. The data show the months of July and August to be exceptional in terms of ozone production efficiency (the gradient of the total oxidant/NO<sub>x</sub>) plot which reflects the much lower daytime traffic activity and emissions of precursor pollutants during these months. There is also a substantial weekday/weekend difference with higher NO<sub>x</sub> concentrations on weekdays accompanied by lower ozone than at weekends. It appears that the reduced titration of ozone with NO and consequent enhanced NO<sub>2</sub>/NO ratio in July and August and at weekends is influencing the photostationary state, but also the oxidant plots suggest enhanced ozone production efficiency at the lower NO<sub>x</sub> concentrations possibly because of the reduced influence of NO<sub>2</sub> and VOC as a sink for free radical species.

455

Overall, the data show the region to be in many ways similar to other areas with high traffic emissions and a photochemically reactive atmosphere, although there are some significant differences associated in the main with cultural factors affecting road traffic emissions. Further studies including both roadside and rural sites would lead to a deeper understanding of the ozone climate of the region. Collection of traffic data, unavailable to this study would also assist in data interpretation.

462

463

464

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608

609

610 **FIGURE LEGENDS**

611

612 **Figure 1:** Map of Jeddah with the sampling site marked with a star. Map data © Google, 2013  
613 Terra Metrics.

614

615 **Figure 2:** Monthly variation of (a) temperature, (b) relative humidity, (c) wind speed and (d)  
616 solar radiation.

617

618 **Figure 3:** Monthly variations of mean daytime and daily concentrations of ozone during th  
619 period of study.

620

621 **Figure 4:** Monthly variations of daytime, nighttime and daily concentrations of NO and NO<sub>2</sub>  
622 during the period of study.

623

624 **Figure 5:** Monthly variations of NO<sub>2</sub>/NO<sub>x</sub> concentration ratios.

625

626 **Figure 6:** Diurnal variations in NO, NO<sub>2</sub> and O<sub>3</sub> concentrations during the different seasons.

627

628 **Figure 7:** Gradient and intercept of a plot of total oxidant (O<sub>3</sub> + NO<sub>2</sub>) versus NO<sub>x</sub> concentration  
629 for daytime samples for each month (equation  $O_x = bNO_x + a$ ).

630

631 **Figure 8:** Diurnal variations of NO and NO<sub>2</sub> concentrations on weekdays and weekends (left  
632 column) and weekday/weekend concentration ratios (right column) during the  
633 different seasons.

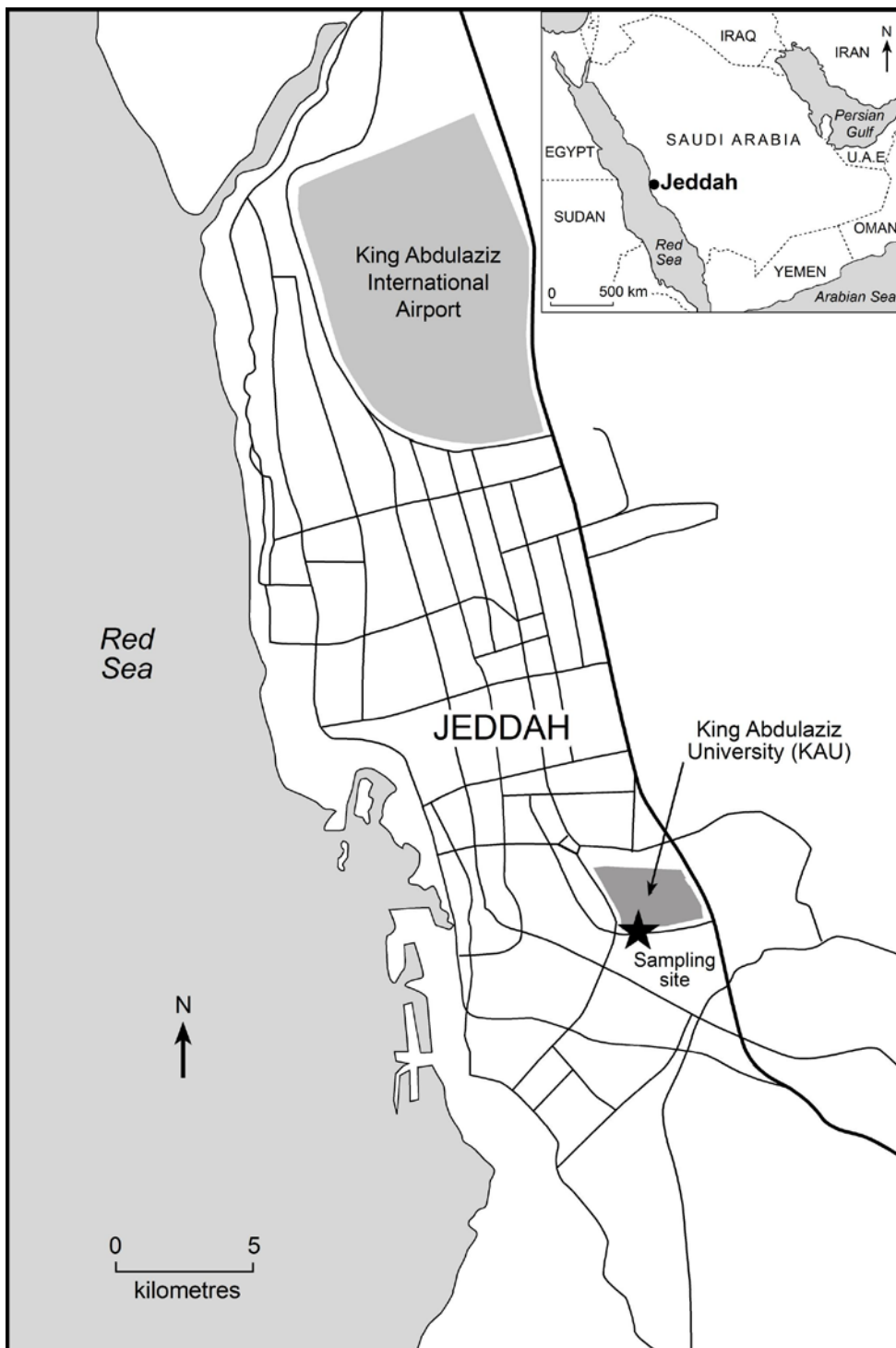
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635 **Figure 9:** Diurnal variations of NO<sub>x</sub> and O<sub>3</sub> on weekdays and weekends and weekend minus  
636 weekday concentrations (ppb) during the different seasons.

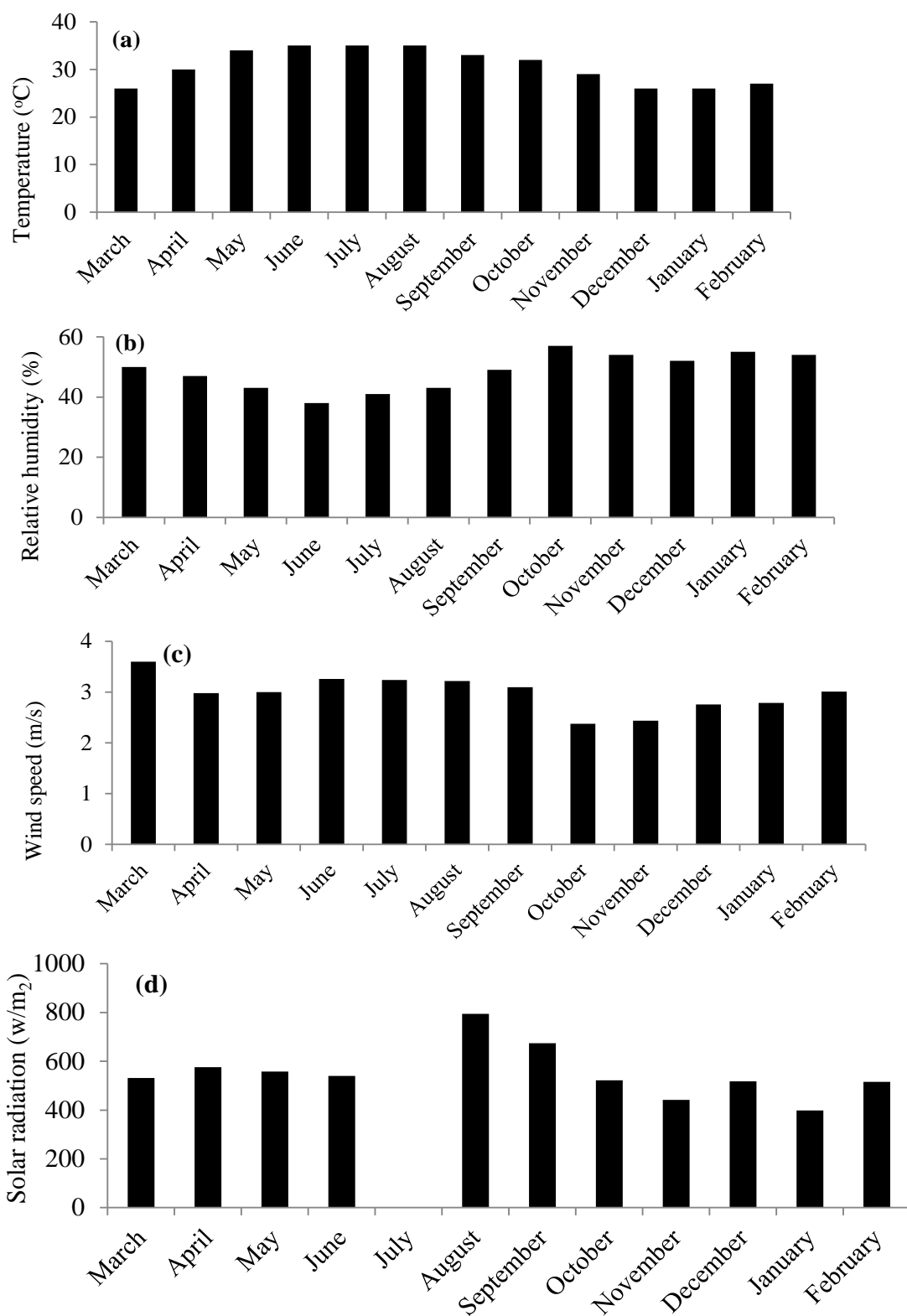
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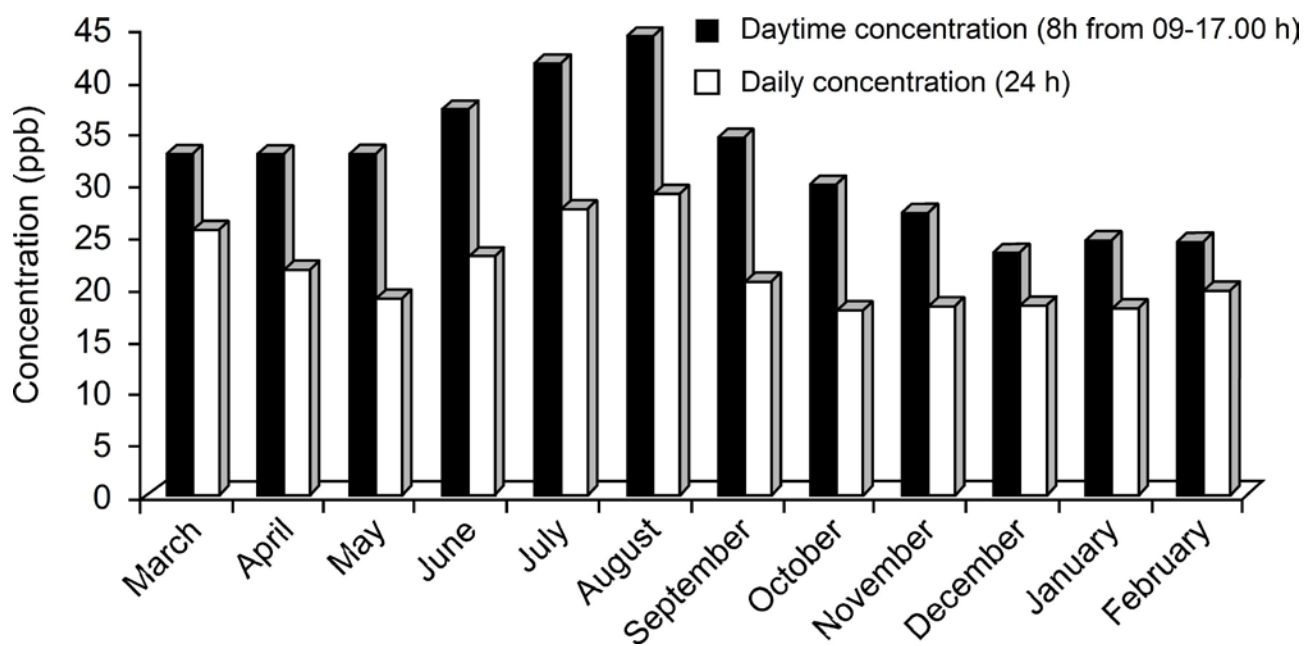


**Figure 1.** Map of Jeddah with the sampling site marked with a star. Map data © Google, 2013  
Terra Metrics



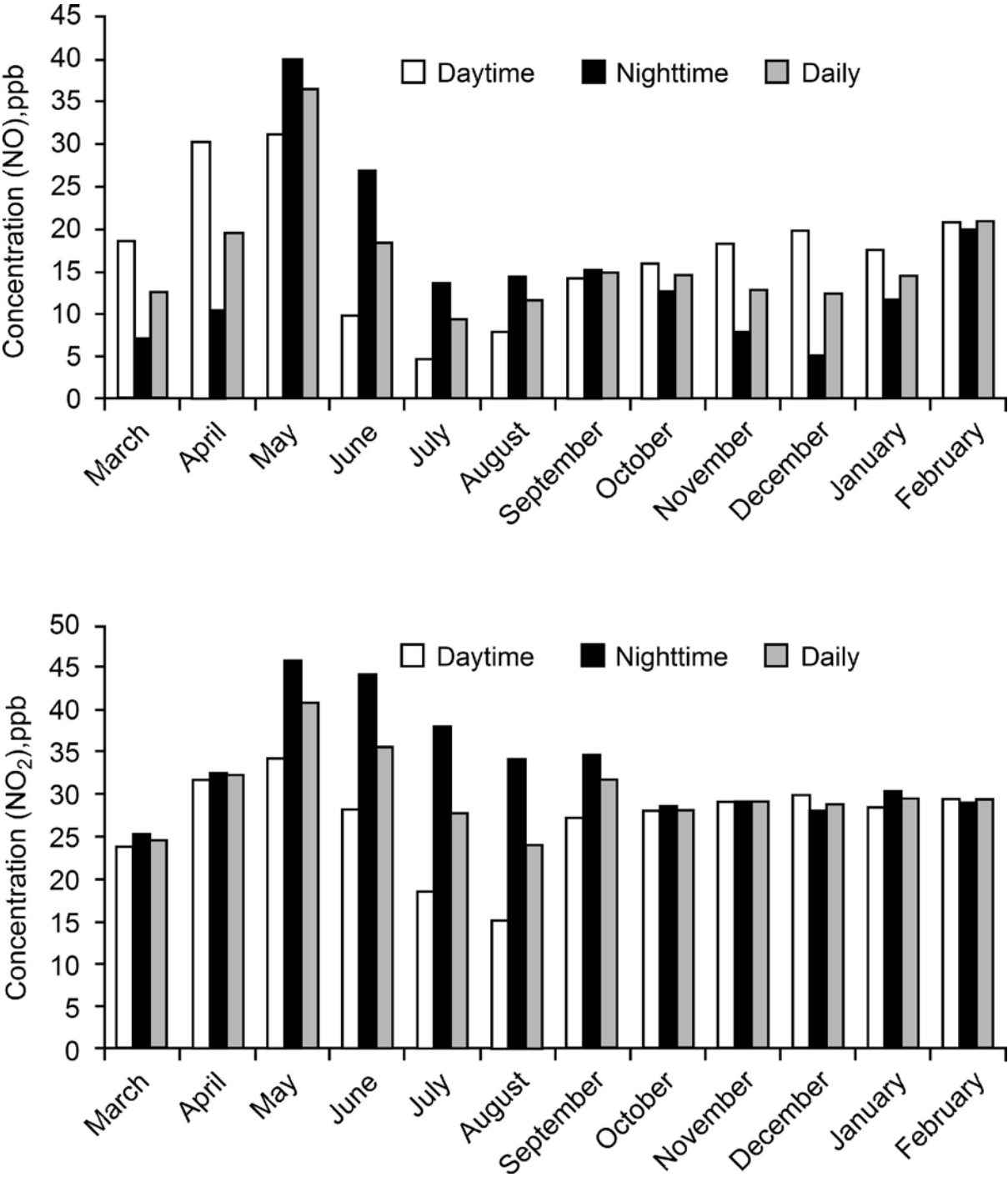
**Figure 2.** Monthly variation of (a) temperature, (b) relative humidity, (c) wind speed and (d) solar radiation





**Figure 3.** Monthly variations of mean daytime and daily concentrations of ozone during the period of study

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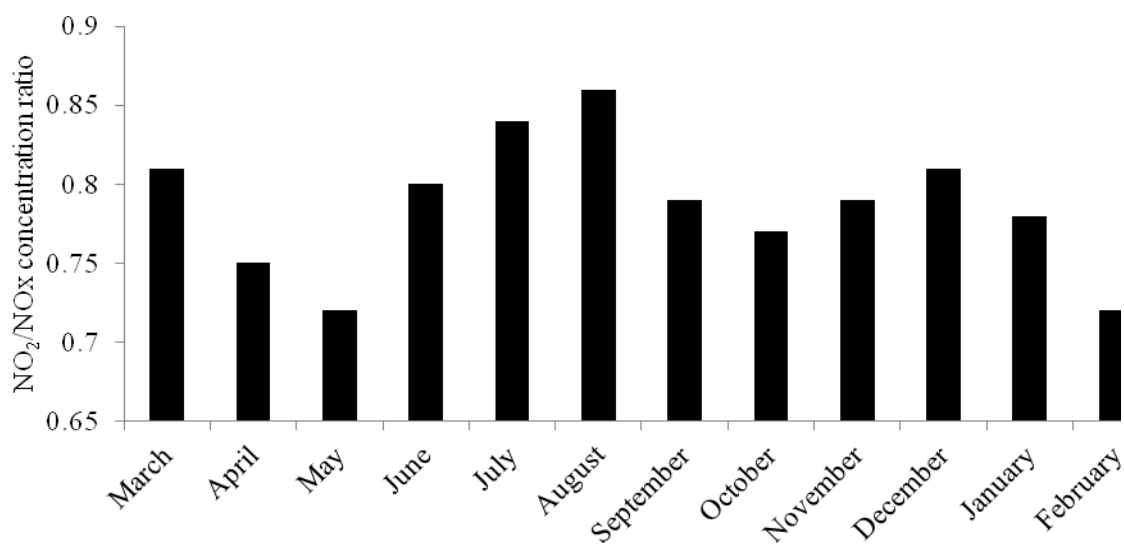
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658 **Figure 4.** Monthly variations of daytime, nighttime and daily concentrations of NO and NO<sub>2</sub> during  
659 the period of study

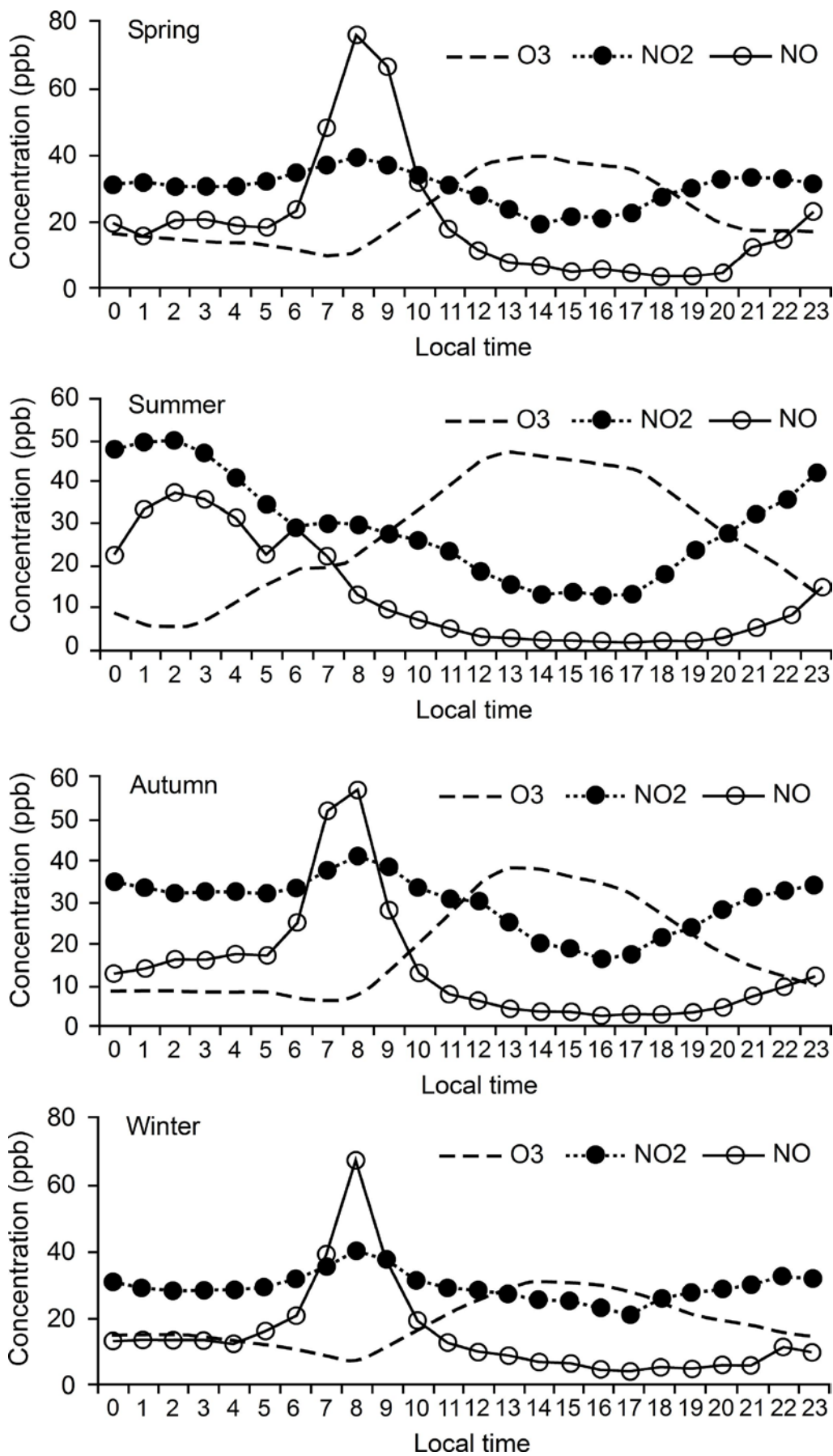
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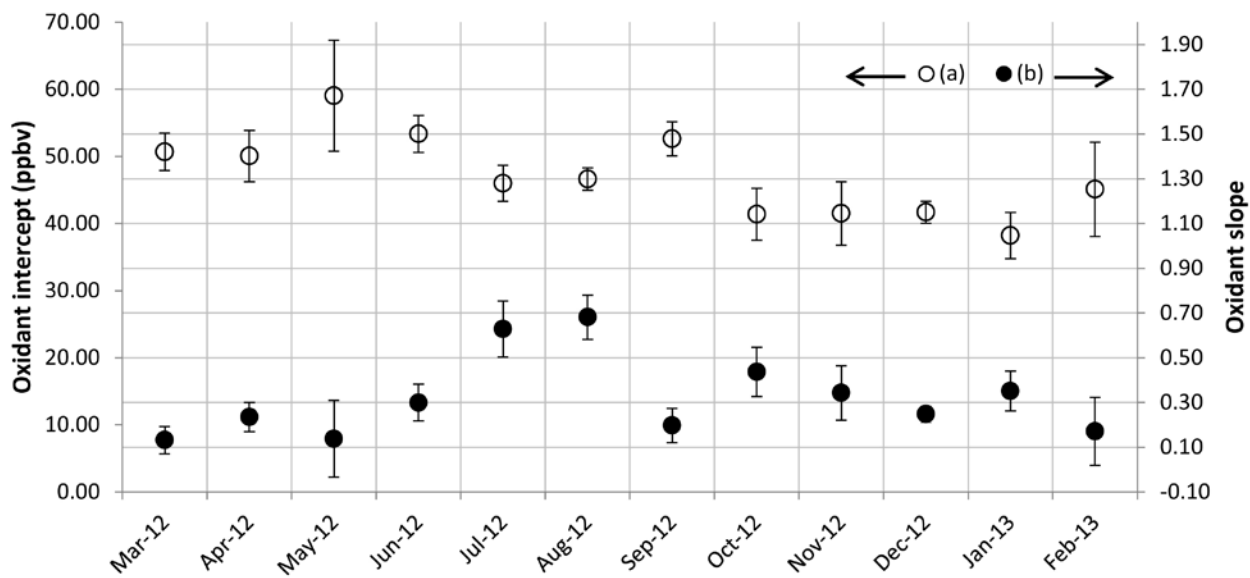
665 **Figure 5.** Monthly variations of NO<sub>2</sub>/NO<sub>x</sub> concentration ratios



666

667

668 **Figure 6.** Diurnal variations in NO, NO<sub>2</sub> and O<sub>3</sub> concentrations during the different seasons



669

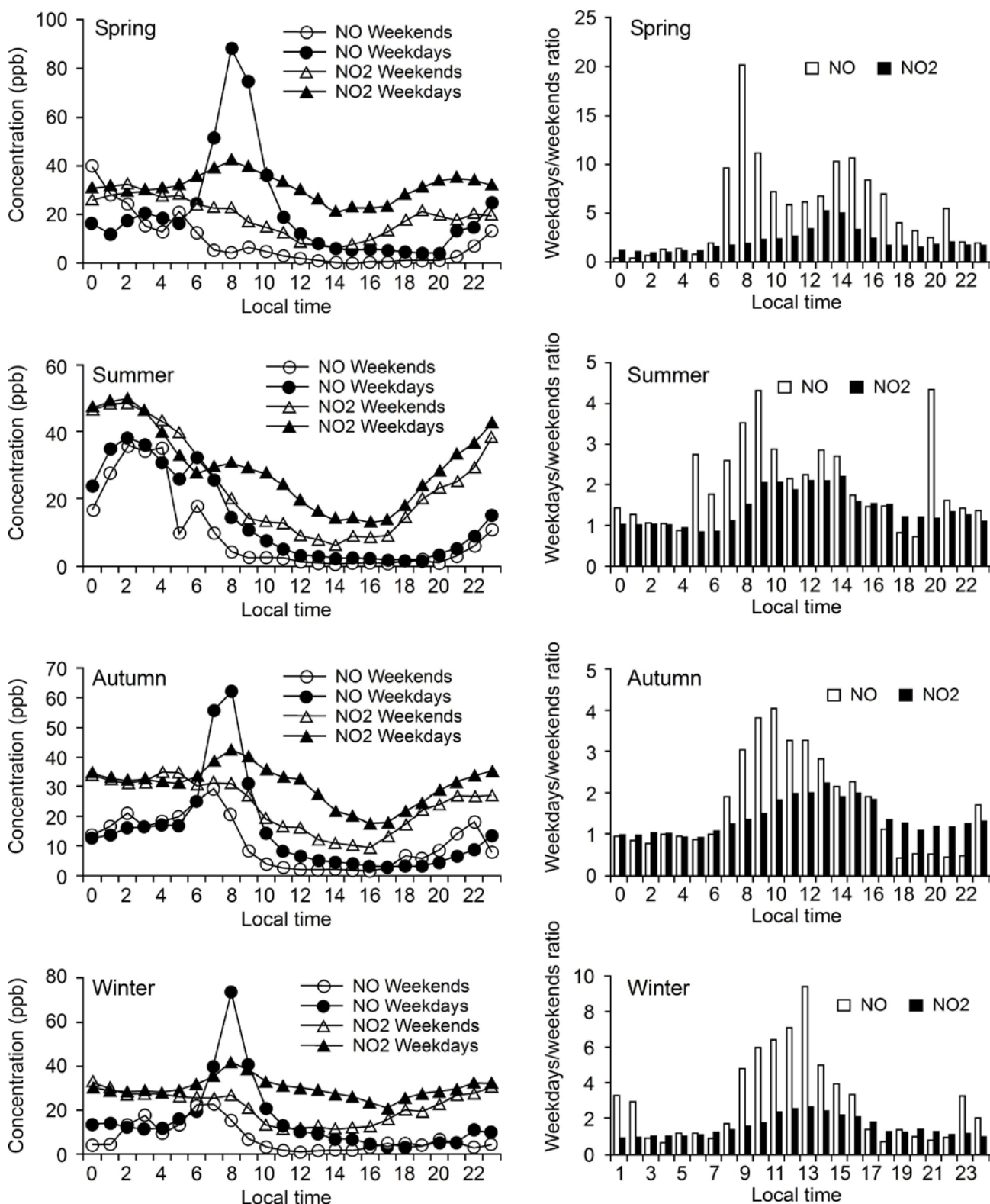
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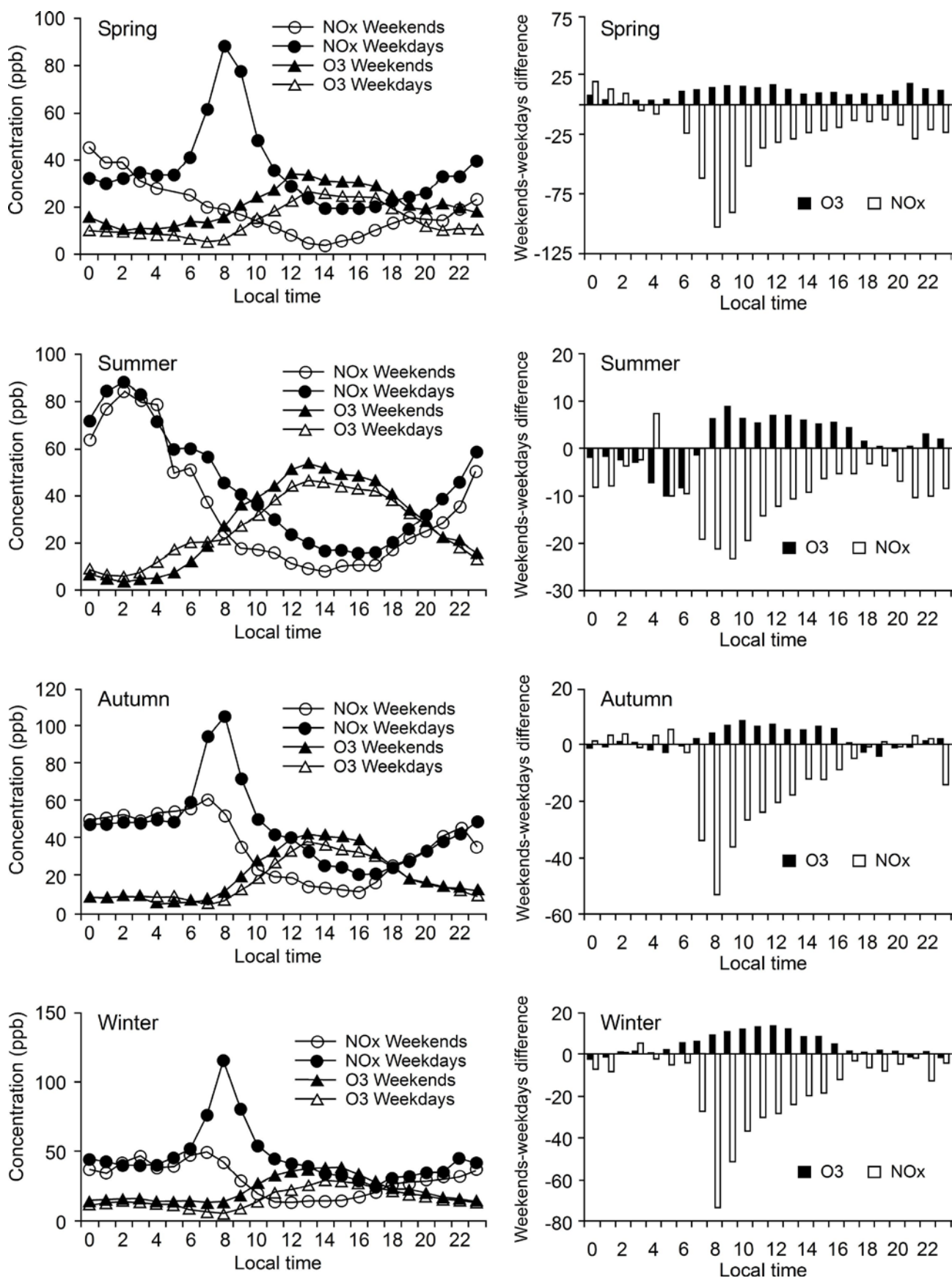
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**Figure 7.** Gradient and intercept of a plot of total oxidant ( $O_3 + NO_2$ ) versus  $NO_x$  concentration for daytime samples for each month (equation  $O_x = bNO_x + a$ )



**Figure 8.** Diurnal variations in NO and NO<sub>2</sub> concentrations on weekdays and weekends (left column) and weekday/weekend concentration ratios (right column) during the different seasons



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681 **Figure 9.** Diurnal variations in  $\text{NO}_x$  and  $\text{O}_3$  on weekdays and weekends, and weekend minus  
 682 weekday concentrations (ppb) during the different seasons

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